Electrochemical Destruction of Short Chain PFAS Compounds from Remediation Waste Streams

Even as EPA restrictions are delayed, still, there's no time to waste. Water agencies can look to optimized boron doped diamond electrodes to deliver highly effective PFAS destruction technologies within treatment trains—here's how.

By Element Six's Bruce Bolliger and Lummus Technology's, Chad Felch, Mark Clark, Conrad Shields

A report by the United States Geological Survey indicated that 45% of drinking water sources tested in the US contained at least one type of per- and polyfluoroalkyl (PFAS) substance, suggesting that contamination of environmental, ground water and waste waters is remarkably pervasive.[1] The link to serious medical conditions of long term bio-accumulation of first generation PFAS has established the drive to remove sources of this contamination.[2] US government regulators, have placed both strict limits on six legacy PFAS compounds together with exposure limits for all PFAS compounds.[3] As stringent requirements for maximum allowable PFAS come into force globally, emerging new remediation processes that remove PFAS from drinking water in turn generate significant new waste streams, containing concentrated PFAS in the μgL^{-1} to mgL^{-1} range.

A significant contributing factor to the proliferation of PFAS in the environment is that existing waste management infrastructure fails to destroy or contain PFAS. Thus, new technology is needed to mitigate the further spread of PFAS into the environment. The most common method for extraction of PFAS from aqueous sources is media adsorption (activated carbon or ion exchange resin). While the adsorbent itself is typically easy to burn, PFAS compounds are difficult to incinerate. Without extraordinary temperatures and specialized off-gas handling, it is likely that PFAS compounds will escape from the stack.[4]

Placing spent adsorbent in landfill instead does not permanently capture the PFAS as over time it will leach out of the resin. There will therefore be a focus on landfills to control the PFAS content of leachates that potentially contaminate the environment.[5] In the case of concentrated PFAS solutions, such as foam fractionates or ion-exchange regeneration solutions, these cannot be disposed of by biological wastewater treatment processes because they do not destroy PFAS compounds.

The recent designation of PFOA and PFOS as hazardous substances by the EPA will further the drive to develop cost-effective destruction technologies.[6] Of necessity is a technology able to destroy PFAS compounds of all carbon chain lengths as a destruction process has the potential to form shorter chain PFAS byproducts that have their own health risks.[7]

Electrochemical destruction of PFAS at the surface of boron doped diamond (BDD) electrodes is one of the most promising techniques for ending the cycle of PFAS contamination for both long- and short-chain PFAS compounds.[8]

With BDD electrodes, however, the near-electrode-surface oxidation requires a minimum PFAS concentration of ~2000 ngL^{-1} for treatment to be economically feasible. Furthermore, BDD electrodes can require for conductivity high levels of total dissolved solids (TDS) that potentially generate harmful byproducts such as perchlorates. These two issues create a significant barrier to a direct-to-discharge treatment system but can be addressed by decoupling the remediation processes from a destruction stage that operates at high current density, high over-potentials, and high pH.

Boron Doped Diamond Electrodes for PFAS Destruction

BDD is a polycrystalline form of synthetic diamond manufactured using the chemical vapor deposition (CVD) process.

A small subset of BDD electrodes is manufactured using microwave CVD diamond with which an order of magnitude higher growth rate is possible. Microwave CVD allows the production of free-standing BDD electrodes at thicknesses that are 0.3 to 2 mm thick and typically 130 to 140 mm in diameter, (surface area >13,000 mm^2). These electrodes exhibit wider solvent windows and low capacitances, primarily due to their larger grain size compared to thin-film BDD electrodes.[9] The absence of a metal substrate also means these free-standing BDD electrodes can be used at extreme pH levels. And with the thicker BDD layer, they can be operated at greater than 10 times higher current densities, up to 30,000 Am^{-2}, for similar or longer lifetimes.[10]

Energy Consumption of Electrochemical Oxidation

Technologies that remove PFAS from water produce waste streams that contain higher concentrations of other organics, typically by at least two orders of magnitude higher than the PFAS. The treatment time for those organics will play a key role in the time taken to successfully treat the waste effluent since the oxidation of PFAS and dissolved organics will occur simultaneously. Electrochemical oxidation cells operate in two different regions, a current-limited region and a mass-transport-limited region. To maintain optimal economics, the electrochemical cell must operate in the current-limited region at concentrations greater than ~2,000 ngL^{-1}.

When operating in the current limited region, the energy consumption of electrochemical advanced oxidation systems is in the region of 20 to 40 $kWhkg^{-1}$ of chemical oxygen demand (COD) removed. While other thermal processes have lower energy consumption, these processes (unless above 370°C and 300 bar (SCWO) or 1400°C for thermal incineration) do not destroy all PFAS, particularly short-chain PFAS ($C \leq 4$).

Removing PFAS From Landfill Leachates

Disposal of products containing PFAS in landfills has resulted in landfill leachate that contains PFAS compounds. Because standard leachate treatment methods do not remove PFAS compounds, the treated leachates are still an environmental liability. In February

2024, the US Environmental Protection Agency proposed changes to the Resource Conservation and Recovery Act (RCRA) adding nine specific per- and polyfluoroalkyl compounds to its list of hazardous constituents. Landfill leachate is likely to contain all of these substances. If the leachate is treated biologically before any PFAS compounds are removed, then both the treated liquid effluent and the resulting biological solids will contain PFAS. For this reason, it is best to treat the leachate for PFAS prior to biological treatment.

Foam fractionation can be effective at removing PFAS from landfill leachates. Foam fractionation produces a very small amount of liquid, often concentrating the PFAS by a couple orders of magnitude. The relatively small amount of liquified foam can then be treated using an electro-oxidation process with BDD electrodes to destroy the PFAS compounds.

Figure 1: Zimpro® electro-oxidation (ZEO) pilot unit.

Case Study Treatments of PFAS in Foam Fractionate from Landfill Leachate

Samples of foam fractionate from a landfill leachate produced using a multistage foam fractionation system were treated using a Zimpro® electro-oxidation (ZEO) pilot unit from Lummus Technology (see Figure 1). The ZEO pilot unit utilises free-standing BDD electrodes from Element Six in a flow through cell configuration, with the effluent making multiple passes. Results from the tests are shown in Table 1. Samples were analyzed using EPA Draft Method 1633. This method analyzes for 40 PFAS compounds, including the nine proposed RCRA PFAS compounds. Over the course of the tests the total PFAS was reduced by 99.996%, with the concentration of all measured compounds substantially reduced, including the short-chain PFAS compounds (e.g. PFBA and PFBS). The total PFAS shows that the rate of oxidation slows down over time due to decreasing concentration and the process being mass transfer limited at low concentrations.

Table 1.

Relat-ive Power	Organ-ic Carbon	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFBS	PFPeS	T-PFHxS	PFHpS	T-PFOS	6:2FTS	5:3FTCA	7:3FTCA	Total PFAS	PFAS Destruct-ion
	mgL^{-1}	ngL^{-1}	ngL^{-1}	ngL^{-1}	ngL^{-1}	ngL^{-1}	ngL^{-1}	ngL^{-1}	ngL^{-1}	ngL^{-1}	ngL^{-1}	ngL^{-1}	ngL^{-1}	ngL^{-1}	ngL^{-1}	ngL^{-1}	
0	336	31,700	88,000	351,800	190,400	193,900	14,000	5,300	20,700	510,200	12,900	387,900	9,347,000	583,900	55,200	11,792,900	
3x		289.6	28.2	28.2	13.7	75.58	<0.797	42.8	1.7	6.8	<0.75	47.4	38.6	<7.97	<7.97	525	99.996%

The test results shown in Table 1 clearly indicate that PFAS, including short-chain PFAS, is destroyed using BDD electrodes at high current density. Only solid BDD electrodes can generate high current densities (> 2,000 Am^{-2}).

Commercial Scale Treatment of PFAS in Foam Fractionate Concentrate

These results from pilot projects have demonstrated that free-standing BDD electrodes can be operated at a very high current density to destroy even small-chain PFAS compounds. As the concentration of PFAS and other organics reduces, the process alters from a relatively energy efficient current limited oxidation region to a far less efficient mass transport limited region. Economics indicates then that the overall process needs to be designed to operate in the energy efficient, current limited region.

When treating landfill leachate, a treatment system would likely consist of a foam fractionator and a ZEO BDD-electrode electro-oxidation based PFAS destruction module. The landfill leachate would be sent to the foam fractionator, and the PFAS containing foam from the fractionation process would then be treated using the electro-oxidation process.

A commercial treatment system would be a semi-batch process where liquid is sent to the system placed in a circulation tank. Once loaded, the PFAS concentrate is pumped across the BDD electrodes where oxidation occurs and then is returned to the circulation tank. In this way, long-chain PFAS compounds are broken apart to become either CO_2, NaF or fractionally smaller PFAS compounds. The longer the process is operated the more oxidation occurs and eventually only the smaller 4 and 5 carbon PFAS compounds remain. To avoid moving into an electrically inefficient region, the partially oxidized PFAS mixture would be re-circulated to the front end of the foam fractionation process. The already treated liquid would be combined with the PFAS directly from the leachate where the foam fractionation process will then again form a concentrated PFAS stream for electro-oxidation treatment. In this way, the electro-oxidation process never produces a completely PFAS-free effluent but when combined with foam fractionation, the overall process produces a low PFAS effluent. The treated effluent can be further polished using AIX (resin ion exchange) to further ensure no short-chain PFAS is returned to the environment.

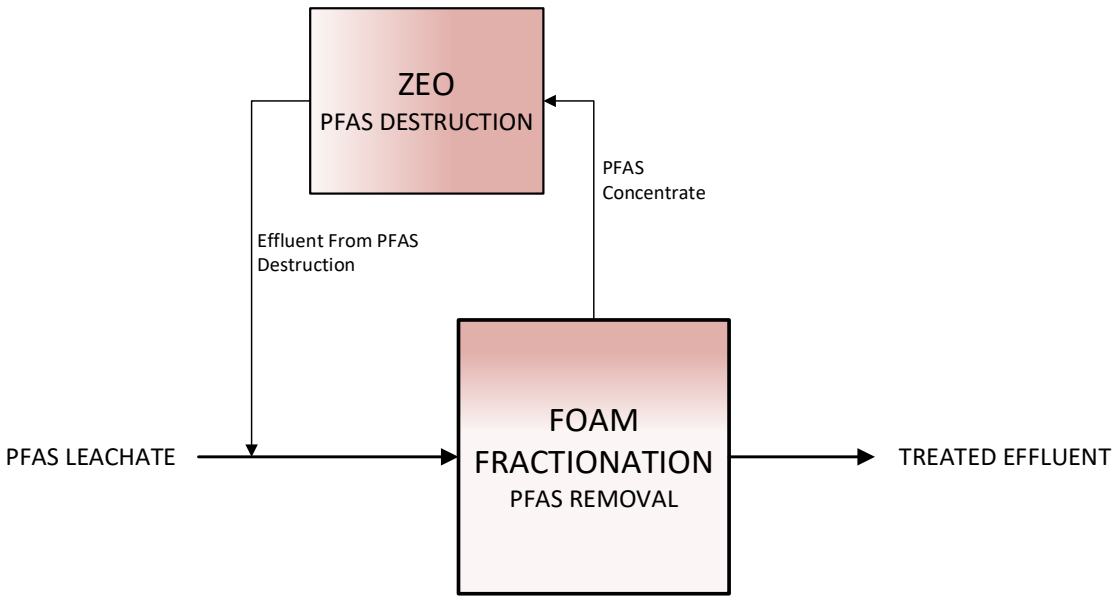

Figure 2: Simple process flow diagram of a PFAS treatment system for landfill leachate.

Preliminary Model and Economics for PFAS Treatment System

Coupling foam fractionation with BDD electro-oxidation promises to be a highly effective and economically practical solution for landfills with PFAS-contaminated leachate. Considering the limited flow of leachate with relatively high concentration of PFAS compounds, it is feasible to implement this technology at the landfill site at a starting cost between $8 and $18.5 m^{-3} of leachate. It could easily be retrofitted to existing landfill leachate treatment systems and scaled to fit leachate volumes.

The Future of PFAS Destruction

As the regulations around PFAS come into place, more attention is being placed on developing PFAS destruction technologies to be implemented with remediation solutions. Electrochemical oxidation processes have advantages of being commercially available and field proven as turnkey, modular in process, and proven to effectively breakdown PFAS compounds at least down to C≤4.

Trials of electro-oxidation reactors employing free-standing BDD electrodes to destroy PFAS show promising results because of their extreme oxidation potential and high current density (> 2000 Am^{-2}) capability. Pilot testing of real-world samples from foam-fractionated landfill leachate prove this technology is capable of destroying even the most stubborn PFAS short-chain (C≤4) compounds. For example, and well-timed with the EPA's recent move to open up the timeline for the exploration and adoption of commercial solutions, Lummus Technology is offering treatment trials of field samples.

PFAS regulations likely will have extremely low () limits. With PFAS being the final compounds to be destroyed, the BDD-based electro-oxidation process alone would not be

cost effective to meet these low discharge limits. Some form of additional separation and concentration of the PFAS compounds will be required to boost the energy efficiency of the process. Although the BDD-based electro-oxidation process is already scaled up for other applications, optimization for typical volumes and organic loads of the effluent streams in PFAS applications is needed via field trials at remediation sites, which are already underway.

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